

TECHNICAL MEMORANDUM



TO: Dennis Crumpler / OAQPS
FROM: Eric Boswell / NAREL
AUTHOR: Steve Taylor
DATE: August 18, 2010
SUBJECT: Gravimetric Inter-Laboratory Comparison Study

Introduction

The EPA's National Air and Radiation Environmental Laboratory (NAREL) conducts semi-annual gravimetric inter-laboratory comparison studies as part of its quality assurance support of EPA's Office of Air Quality Planning and Standards (OAQPS). The purpose of the gravimetric studies is to evaluate selected EPA and State laboratories that weigh Teflon® filters used for the determination of PM_{2.5} collected with Federal Reference Method (FRM) ambient air samplers. Results for the second study of 2010 have been submitted by participating laboratories. EPA labs that participated in this study were the Region 4 laboratory in Athens, GA and the Radiation and Indoor Environments Laboratory (R&IE) in Las Vegas, NV. The Region 4 laboratory provides pre- and post-weighing of filters for the PM_{2.5} Performance Evaluation Program (PEP). The R&IE Laboratory provides pre- and post- weighing of Teflon® filters in support of the Tribal Air Monitoring Support (TAMS) PM_{2.5} air monitoring program. Two State laboratories, Maryland's Department of Health and Mental Hygiene (DHMH) and the Puerto Rico Environmental Quality Board (PREQB) were also included in this study. NAREL coordinated this study by supplying performance evaluation (PE) samples and served as the reference laboratory.

Mass determination of PM_{2.5} is performed using a microbalance to weigh the Teflon® collection filter before and after the sampling event. The amount of particulate matter (PM_{2.5}) captured onto the surface of the filter can be calculated by a simple subtraction of the tare or pre-mass from the loaded filter or post-mass. In order to accurately measure particulate mass at microgram levels, the microbalance must be located in a clean, dust free environmental chamber with precise temperature and humidity control. Elimination of static from samples is also very important for accurate mass measurements.

The laboratories participating in this study are equipped with microbalances capable of mass measurements of one microgram sensitivity. All laboratories in this study perform mass measurements inside environmentally controlled weighing rooms in order to maintain a constant temperature and humidity and to control dust contamination.

Samples for this study were created at NAREL using three co-located Met One Super SASS air samplers to collect various amounts of PM_{2.5} onto Teflon® filters. In addition to the loaded filter samples, blank filters and metallic weights were included as controls and to provide information concerning balance stability and calibration. This study compares captured mass determined by NAREL to captured mass determined by each of the participating laboratories.

Acceptance criteria for this type of comparison have not been established. There are PEP criteria established for laboratory and field blanks, and metallic standards. According to the PEP criteria, laboratory and field blanks should not vary by more than 0.015 mg and 0.030 mg respectively between pre- and post-measurements. Metallic standards should not vary by more than 0.003 mg. As an alternative to the PEP criteria, this study uses acceptance limits based on actual mass data compiled from past gravimetric PT studies administered by NAREL.

Experimental

To begin this study, four sample sets consisting of ten new Teflon® filters and two metallic weights were assembled. Each filter was carefully inspected using a light table to check for pinholes and fibers. The metallic weights were commercially available 100 and 200 milligram stainless steel weights that were slightly altered by clipping a small corner section from each weight. The samples were equilibrated in NAREL's weighing chamber and weighed before they were shipped to each laboratory with instructions to equilibrate and tare the samples following their standard operating procedures for the determination of PM_{2.5} mass. The laboratories were asked to complete this part of the study in approximately one week from receipt of the samples. As each sample set was returned to NAREL, filters were again inspected for pinholes and visible contamination and then allowed to equilibrate overnight in the weighing chamber. Following overnight equilibration, the filters were weighed to determine NAREL's pre-mass of record. After the NAREL pre-masses were established for all samples, seven filters from each set of ten were loaded with PM_{2.5} collected from the ambient air at NAREL. The remaining filters from each set were utilized as blanks.

Four sampling events using co-located Met One Super SASS air samplers were used to load the Teflon® filters. The first event ran 48 hours and loaded two filters from each set. A second 30 hour event loaded one filter from each set. A third and fourth event of 24 hours and 20 hours loaded two additional pairs of filters from each set. The three remaining filters from each set of ten served as blanks. Sampling events are summarized in table 10.

Following each collection event, samples were returned to NAREL's weighing chamber for equilibration. Once the filters were loaded and equilibrated, the first post-mass measurements were made. The filters were given an additional four days to equilibrate and all samples were weighed again. Mass results of this last weigh session became NAREL's post-mass of record for this study.

Following the post-mass determinations, each sample set was placed into a cooler containing substitute ice and a letter of instructions. The coolers were shipped to the participating laboratories by next day air.

Instructions provided with the samples allowed laboratories two weeks from the time of receipt to obtain their post-mass measurements and return the samples back to NAREL.

Gravimetric Results

Figure 1 presents the inter-laboratory capture differences for all samples. As stated earlier, the capture is calculated by subtracting the pre-mass from the post-mass. Inter-laboratory differences were calculated by subtracting the capture value reported by the test laboratory from the capture value determined at NAREL. The negative bars shown in Figure 1 indicate that the test lab capture was larger than NAREL's capture. The absence of a bar indicates perfect agreement with NAREL. The advisory limits shown in Figure 1 are 3-sigma limits derived from all gravimetric PT studies administered by NAREL during the past several years.

Metallic weights were included in this study because they are more stable than a Teflon® filter, especially a loaded Teflon® filter. The metallic weights were weighed at each laboratory during the initial tare sessions as well as during the final loaded sessions. The difference in initial and final mass is the calculated “mass capture” for the metallic weights. Ideally, the “mass capture” for the metallic weight samples would be zero. A large difference between an initial and final mass could indicate a balance stability or calibration problem.

Figure 1

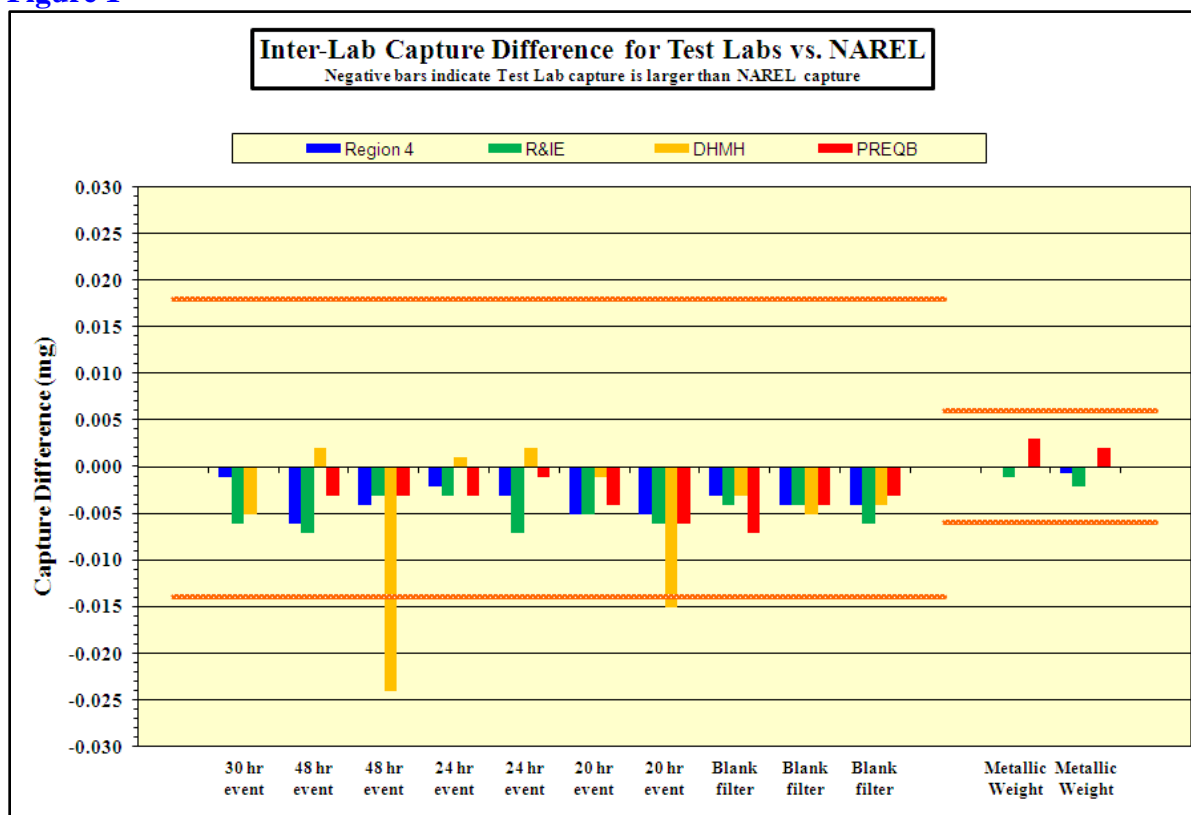


Figure 1 shows that except for two outliers, results of the inter-lab comparisons for the Teflon® filters and metallic samples were within the 3 sigma advisory limits. The two outliers shown in figure 1 indicate that the participating lab's capture was 24.0 µg and 15 µg larger than NAREL's capture respectively.

To investigate possible causes for the two outlier results, all sample sets were reweighed at NAREL and the results compared to the post-mass of record results. Table 1 shows NAREL's mass results for the sample set that contained the two outlier filters (T10-13290 and T10-13294) shown in figure 1. The data include NAREL's tare mass of record, the post-mass of record and

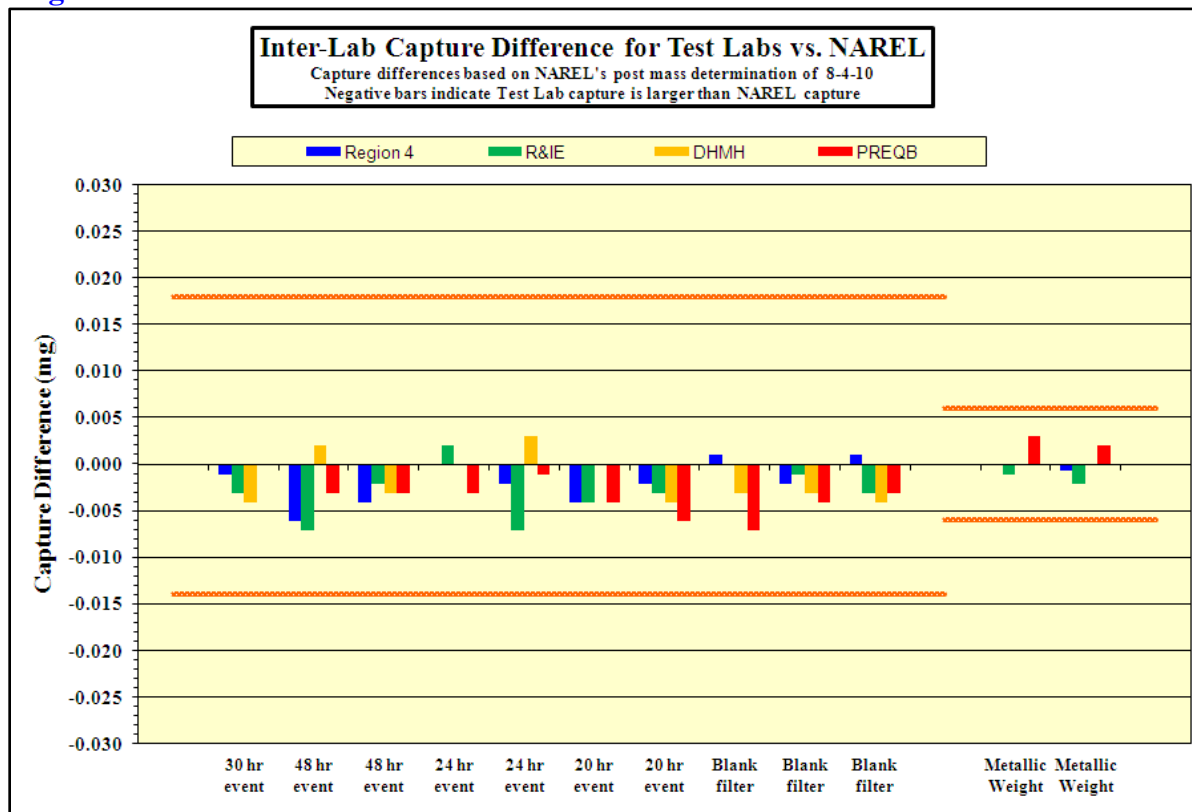
the additional post-mass determined after the samples were returned at the end of the study. Table 1 shows that the two filters in question (T10-13290 and T10-13294) gained 21 and 11 μg respectively

Table 1.

Sample ID	Pre-mass of record (6-28-10) (mg)	Post-mass of record (7-19-10) (mg)	Additional Post-mass (8-4-10) (mg)	Difference (mg)
T10-13288	146.874	147.067	147.068	0.001
T10-13289	145.531	145.868	145.868	0.000
T10-13290	145.279	145.622	145.643	0.021
T10-13291	149.812	149.976	149.975	-0.001
T10-13292	144.100	144.264	144.265	0.001
T10-13293	146.783	146.952	146.953	0.001
T10-13294	147.190	147.349	147.360	0.011
T10-13295	145.884	145.885	145.885	0.000
T10-13296	148.775	148.775	148.777	0.002
T10-13297	146.700	146.699	146.699	0.000
MW10-13316	181.334	181.334	181.334	0.000
MW10-13317	93.776	93.776	93.776	0.000

All NAREL mass captures were recalculated using the post-masses determined on 8-4-10. Figure 2 shows the recalculated inter-lab capture differences.

Figure 2



As figure 2 illustrates, all comparisons are well within advisory limits.

The raw data reported from all laboratories have been tabulated in Tables 2 - 9 at the end of this report. Tables 2-5 contain the NAREL's pre-mass of record, post-mass of record, and the calculated PM_{2.5} capture. Tables 6-9 contain NAREL's additional post-mass measurements with recalculated mass capture and inter-lab differences determined at the end of the study.

Conclusions

This study evaluated laboratories that perform gravimetric measurements of 47-mm Teflon® filter samples used to collect PM_{2.5}. Samples for this study were created at NAREL by loading Teflon® filters with PM_{2.5} collected from the ambient air. Blank filters and metallic weights were also included as samples. Each laboratory was allowed to pre-weigh and post-weigh a unique set of samples in order to determine the mass capture for each sample. Performance was evaluated by comparing mass capture results produced by NAREL to results produced by each test laboratory. This method eliminates slight differences in balance calibration and environmental conditions among different laboratories since both pre- and post- weights are determined at each location using the same balance. This study showed very good inter-laboratory agreement for the majority of the mass measurements. Two of the filter comparison results exceeded the advisory limits set for the study. As further investigation, an additional post weighing of all samples was performed at NAREL at the end of the study. Results of the final weighing showed that the two filters in question had gained significant mass when compared to the post-mass of record; however, it is not possible to determine the cause of the mass gain. All NAREL mass capture results and all inter-lab capture differences were recalculated based on the new measurements. Based on these new measurements, all inter-laboratory comparisons showed very good agreement.

Table 2. Gravimetric Data Region 4

Sample ID	Pre-Mass		Post-Mass		Captured PM2.5		Inter-Lab Difference* of Captured PM2.5 (mg)	Sampling Duration Hours
	Region 4 (mg)	NAREL (mg)	Region 4 (mg)	NAREL (mg)	Region 4 (mg)	NAREL (mg)		
T10-13255	147.727	147.724	147.927	147.923	0.200	0.199	-0.001	30 hr
T10-13249	148.669	148.668	149.013	149.006	0.344	0.338	-0.006	48 hr
T10-13250	149.543	149.540	149.888	149.881	0.345	0.341	-0.004	48 hr
T10-13251	143.410	143.407	143.574	143.569	0.164	0.162	-0.002	24 hr
T10-13252	144.278	144.275	144.443	144.437	0.165	0.162	-0.003	24 hr
T10-13253	151.269	151.267	151.431	151.424	0.162	0.157	-0.005	20 hr
T10-13254	148.474	148.471	148.642	148.634	0.168	0.163	-0.005	20 hr
T10-13248	145.947	145.945	145.947	145.942	0.000	-0.003	-0.003	Blank
T10-13256	148.588	148.585	148.591	148.584	0.003	-0.001	-0.004	Blank
T10-13257	152.141	152.137	152.143	152.135	0.002	-0.002	-0.004	Blank
MW10-13308	180.867	180.867	180.867	180.867	0.000	0.000	0.000	
MW10-13309	91.557	91.560	91.557	91.559	0.000	-0.001	-0.001	
* Negative values indicate a larger capture determined by test lab								

Table 3. Gravimetric Data R&IE

Sample ID	Pre-Mass		Post-Mass		Captured PM2.5		Inter-Lab Difference* of Captured PM2.5 (mg)	Sampling Duration Hours
	R&IE (mg)	NAREL (mg)	R&IE (mg)	NAREL (mg)	R&IE (mg)	NAREL (mg)		
T10-13268	147.106	147.099	147.307	147.294	0.201	0.195	-0.006	30 hr
T10-13269	145.331	145.323	145.707	145.692	0.376	0.369	-0.007	48 hr
T10-13270	148.427	148.418	148.772	148.760	0.345	0.342	-0.003	48 hr
T10-13271	146.551	146.542	146.726	146.714	0.175	0.172	-0.003	24 hr
T10-13272	141.561	141.553	141.732	141.717	0.171	0.164	-0.007	24 hr
T10-13273	147.030	147.021	147.202	147.188	0.172	0.167	-0.005	20 hr
T10-13274	147.825	147.816	147.989	147.974	0.164	0.158	-0.006	20 hr
T10-13275	145.772	145.764	145.775	145.763	0.003	-0.001	-0.004	Blank
T10-13276	145.032	145.026	145.036	145.026	0.004	0.000	-0.004	Blank
T10-13277	149.970	149.963	149.975	149.962	0.005	-0.001	-0.006	Blank
MW10-13312	190.083	190.084	190.084	190.084	0.001	0.000	-0.001	
MW10-13313	87.550	87.550	87.552	87.550	0.002	0.000	-0.002	
* Negative values indicate a larger capture determined by test lab								

Table 4. Gravimetric Data DHMH

Sample ID	Pre-Mass		Post-Mass		Captured PM2.5		Inter-Lab Difference* of Captured PM2.5 (mg)	Sampling Duration Hours
	DHMH (mg)	NAREL (mg)	DHMH (mg)	NAREL (mg)	DHMH (mg)	NAREL (mg)		
T10-13288	146.864	146.874	147.062	147.067	0.198	0.193	-0.005	30 hr
T10-13289	145.522	145.531	145.857	145.868	0.335	0.337	0.002	48 hr
T10-13290	145.270	145.279	145.637	145.622	0.367	0.343	-0.024	48 hr
T10-13291	149.801	149.812	149.964	149.976	0.163	0.164	0.001	24 hr
T10-13292	144.090	144.100	144.252	144.264	0.162	0.164	0.002	24 hr
T10-13293	146.774	146.783	146.944	146.952	0.170	0.169	-0.001	20 hr
T10-13294	147.180	147.190	147.354	147.349	0.174	0.159	-0.015	20 hr
T10-13295	145.875	145.884	145.879	145.885	0.004	0.001	-0.003	Blank
T10-13296	148.766	148.775	148.771	148.775	0.005	0.000	-0.005	Blank
T10-13297	146.690	146.700	146.693	146.699	0.003	-0.001	-0.004	Blank
MW10-13316	181.334	181.334	181.334	181.334	0.000	0.000	0.000	
MW10-13317	93.775	93.776	93.775	93.776	0.000	0.000	0.000	
* Negative values indicate a larger capture determined by test lab								

Table 5. Gravimetric Data PREQB

Sample ID	Pre-Mass		Post-Mass		Captured PM2.5		Inter-Lab Difference* of Captured PM2.5 (mg)	Sampling Duration Hours
	PREQB (mg)	NAREL (mg)	PREQB (mg)	NAREL (mg)	PREQB (mg)	NAREL (mg)		
T10-13298	147.779	147.782	147.978	147.981	0.199	0.199	0.000	30 hr
T10-13299	153.204	153.206	153.553	153.552	0.349	0.346	-0.003	48 hr
T10-13300	149.811	149.815	150.183	150.184	0.372	0.369	-0.003	48 hr
T10-13301	147.494	147.498	147.665	147.666	0.171	0.168	-0.003	24 hr
T10-13302	151.177	151.178	151.347	151.347	0.170	0.169	-0.001	24 hr
T10-13303	148.022	148.024	148.190	148.188	0.168	0.164	-0.004	20 hr
T10-13304	150.050	150.053	150.218	150.215	0.168	0.162	-0.006	20 hr
T10-13305	146.622	146.629	146.630	146.630	0.008	0.001	-0.007	Blank
T10-13306	152.184	152.187	152.189	152.188	0.005	0.001	-0.004	Blank
T10-13307	148.048	148.052	148.051	148.052	0.003	0.000	-0.003	Blank
MW10-13318	193.822	193.822	193.820	193.823	-0.002	0.001	0.003	
MW10-13319	92.958	92.959	92.957	92.960	-0.001	0.001	0.002	
* Negative values indicate a larger capture determined by test lab								

Table 6. Gravimetric Data Region 4 and NAREL's additional post-mass results

Sample ID	Pre-Mass		Post-Mass		Captured PM2.5		Inter-Lab Difference** of Captured PM2.5 (mg)	Sampling Duration Hours
	Region 4 (mg)	NAREL (mg)	Region 4 (mg)	NAREL* (mg)	Region 4 (mg)	NAREL (mg)		
T10-13255	147.727	147.724	147.927	147.923	0.200	0.199	-0.001	30 hr
T10-13249	148.669	148.668	149.013	149.006	0.344	0.338	-0.006	48 hr
T10-13250	149.543	149.540	149.888	149.881	0.345	0.341	-0.004	48 hr
T10-13251	143.410	143.407	143.574	143.571	0.164	0.164	0.000	24 hr
T10-13252	144.278	144.275	144.443	144.438	0.165	0.163	-0.002	24 hr
T10-13253	151.269	151.267	151.431	151.425	0.162	0.158	-0.004	20 hr
T10-13254	148.474	148.471	148.642	148.637	0.168	0.166	-0.002	20 hr
T10-13248	145.947	145.945	145.947	145.946	0.000	0.001	0.001	Blank
T10-13256	148.588	148.585	148.591	148.586	0.003	0.001	-0.002	Blank
T10-13257	152.141	152.137	152.143	152.140	0.002	0.003	0.001	Blank
MW10-13308	180.867	180.867	180.867	180.867	0.000	0.000	0.000	
MW10-13309	91.557	91.560	91.557	91.559	0.000	-0.001	-0.001	
* NAREL post-mass determination performed after participating lab determination.								
** Negative values indicate a larger capture determined by test lab								

Table 7. Gravimetric Data R&IE and NAREL's additional post-mass results

Sample ID	Pre-Mass		Post-Mass		Captured PM2.5		Inter-Lab Difference** of Captured PM2.5 (mg)	Sampling Duration Hours
	R&IE (mg)	NAREL (mg)	R&IE (mg)	NAREL* (mg)	R&IE (mg)	NAREL (mg)		
T10-13268	147.106	147.099	147.307	147.297	0.201	0.198	-0.003	30 hr
T10-13269	145.331	145.323	145.707	145.692	0.376	0.369	-0.007	48 hr
T10-13270	148.427	148.418	148.772	148.761	0.345	0.343	-0.002	48 hr
T10-13271	146.551	146.542	146.726	146.719	0.175	0.177	0.002	24 hr
T10-13272	141.561	141.553	141.732	141.717	0.171	0.164	-0.007	24 hr
T10-13273	147.030	147.021	147.202	147.189	0.172	0.168	-0.004	20 hr
T10-13274	147.825	147.816	147.989	147.977	0.164	0.161	-0.003	20 hr
T10-13275	145.772	145.764	145.775	145.767	0.003	0.003	0.000	Blank
T10-13276	145.032	145.026	145.036	145.029	0.004	0.003	-0.001	Blank
T10-13277	149.970	149.963	149.975	149.965	0.005	0.002	-0.003	Blank
MW10-13312	190.083	190.084	190.084	190.084	0.001	0.000	-0.001	
MW10-13313	87.550	87.550	87.552	87.550	0.002	0.000	-0.002	
* NAREL post-mass determination performed after participating lab determination.								
** Negative values indicate a larger capture determined by test lab								

Table 8. Gravimetric Data DHMH and NAREL's additional post-mass results

Sample ID	Pre-Mass		Post-Mass		Captured PM2.5		Inter-Lab Difference** of Captured PM2.5 (mg)	Sampling Duration Hours
	DHMH (mg)	NAREL (mg)	DHMH (mg)	NAREL* (mg)	DHMH (mg)	NAREL (mg)		
T10-13288	146.864	146.874	147.062	147.068	0.198	0.194	-0.004	30 hr
T10-13289	145.522	145.531	145.857	145.868	0.335	0.337	0.002	48 hr
T10-13290	145.270	145.279	145.637	145.643	0.367	0.364	-0.003	48 hr
T10-13291	149.801	149.812	149.964	149.975	0.163	0.163	0.000	24 hr
T10-13292	144.090	144.100	144.252	144.265	0.162	0.165	0.003	24 hr
T10-13293	146.774	146.783	146.944	146.953	0.170	0.170	0.000	20 hr
T10-13294	147.180	147.190	147.354	147.360	0.174	0.170	-0.004	20 hr
T10-13295	145.875	145.884	145.879	145.885	0.004	0.001	-0.003	Blank
T10-13296	148.766	148.775	148.771	148.777	0.005	0.002	-0.003	Blank
T10-13297	146.690	146.700	146.693	146.699	0.003	-0.001	-0.004	Blank
MW10-13316	181.334	181.334	181.334	181.334	0.000	0.000	0.000	
MW10-13317	93.775	93.776	93.775	93.776	0.000	0.000	0.000	
* NAREL post-mass determination performed after participating lab determination.								
** Negative values indicate a larger capture determined by test lab								

Table 9. Gravimetric Data PREQB and NAREL's additional post-mass results

Sample ID	Pre-Mass		Post-Mass		Captured PM2.5		Inter-Lab Difference** of Captured PM2.5 (mg)	Sampling Duration Hours
	PREQB (mg)	NAREL (mg)	PREQB (mg)	NAREL* (mg)	PREQB (mg)	NAREL (mg)		
T10-13298	147.779	147.782	147.978	147.981	0.199	0.199	0.000	30 hr
T10-13299	153.204	153.206	153.553	153.555	0.349	0.349	0.000	48 hr
T10-13300	149.811	149.815	150.183	150.184	0.372	0.369	-0.003	48 hr
T10-13301	147.494	147.498	147.665	147.666	0.171	0.168	-0.003	24 hr
T10-13302	151.177	151.178	151.347	151.347	0.170	0.169	-0.001	24 hr
T10-13303	148.022	148.024	148.190	148.189	0.168	0.165	-0.003	20 hr
T10-13304	150.050	150.053	150.218	150.217	0.168	0.164	-0.004	20 hr
T10-13305	146.622	146.629	146.630	146.632	0.008	0.003	-0.005	Blank
T10-13306	152.184	152.187	152.189	152.191	0.005	0.004	-0.001	Blank
T10-13307	148.048	148.052	148.051	148.054	0.003	0.002	-0.001	Blank
MW10-13318	193.822	193.822	193.820	193.822	-0.002	0.000	0.002	
MW10-13319	92.958	92.959	92.957	92.960	-0.001	0.001	0.002	
* NAREL post-mass determination performed after participating lab determination.								
** Negative values indicate a larger capture determined by test lab								

Table 10. Sampling Schedule

Sample ID	Filter SN	Event Start	Event Duration (hr)	Receiving Lab	Filter Condition
T10-13248	T7105201		Blank	Region 4	Small pinhole
T10-13249	T7105202	7/8/2010	48 hr	Region 4	OK
T10-13250	T7105203	7/8/2010	48 hr	Region 4	OK
T10-13251	T7105204	7/11/2010	24 hr	Region 4	OK
T10-13252	T7105205	7/11/2010	24 hr	Region 4	OK
T10-13253	T7105206	7/12/2010	20 hr	Region 4	OK
T10-13254	T7105207	7/12/2010	20 hr	Region 4	OK
T10-13255	T7105208	7/9/2010	30 hr	Region 4	OK
T10-13256	T7105209		Blank	Region 4	OK
T10-13257	T7105210		Blank	Region 4	OK
T10-13268	T7105221	7/9/2010	30 hr	R&IE	OK
T10-13269	T7105222	7/8/2010	48 hr	R&IE	OK
T10-13270	T7105223	7/8/2010	48 hr	R&IE	OK
T10-13271	T7105224	7/11/2010	24 hr	R&IE	OK
T10-13272	T7105225	7/11/2010	24 hr	R&IE	OK
T10-13273	T7105226	7/12/2010	20 hr	R&IE	OK
T10-13274	T7105227	7/12/2010	20 hr	R&IE	OK
T10-13275	T7105228		Blank	R&IE	OK
T10-13276	T7105229		Blank	R&IE	OK
T10-13277	T7105230		Blank	R&IE	OK
T10-13288	T7105241	7/9/2010	30 hr	DHMH	OK
T10-13289	T7105242	7/8/2010	48 hr	DHMH	OK
T10-13290	T7105243	7/8/2010	48 hr	DHMH	OK
T10-13291	T7105244	7/11/2010	24 hr	DHMH	OK
T10-13292	T7105245	7/11/2010	24 hr	DHMH	OK
T10-13293	T7105246	7/12/2010	20 hr	DHMH	OK
T10-13294	T7105247	7/12/2010	20 hr	DHMH	OK
T10-13295	T7105248		Blank	DHMH	OK
T10-13296	T7105249		Blank	DHMH	OK
T10-13297	T7105250		Blank	DHMH	OK
T10-13298	T7105251	7/9/2010	30 hr	PREQB	OK
T10-13299	T7105252	7/8/2010	48 hr	PREQB	OK
T10-13300	T7105253	7/8/2010	48 hr	PREQB	OK
T10-13301	T7105254	7/11/2010	24 hr	PREQB	OK
T10-13302	T7105255	7/11/2010	24 hr	PREQB	OK
T10-13303	T7105256	7/12/2010	20 hr	PREQB	OK
T10-13304	T7105257	7/12/2010	20 hr	PREQB	OK
T10-13305	T7105258		Blank	PREQB	OK
T10-13306	T7105259		Blank	PREQB	OK
T10-13307	T7105260		Blank	PREQB	OK